

PB-215 467

THE USE OF ULTRAVIOLET ABSORBANCE FOR
MONITORING THE TOTAL ORGANIC CARBON
CONTENT OF WATER AND WASTEWATER

Richard A. Dobbs, et al

Federal Water Pollution Control Administration
Cincinnati, Ohio

May 1969

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 215 467

THE USE OF ULTRAVIOLET ABSORBANCE FOR MONITORING THE TOTAL ORGANIC
CARBON CONTENT OF WATER AND WASTEWATER

Richard A. Dobbs, Robert H. Wise and Robert B. Dean

U. S. Department of the Interior
Federal Water Pollution Control Administration
Advanced Waste Treatment Research Laboratory
Cincinnati, Ohio
May 1969

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

THE USE OF ULTRAVIOLET ABSORBANCE FOR MONITORING THE TOTAL
ORGANIC CARBON CONTENT OF WATER AND WASTEWATER

ABSTRACT

The correlation between ultraviolet absorbance at 254 m μ ($A_{254 \text{ m}\mu}$) and total organic carbon (TOC) content has been determined for a variety of treated and untreated water samples. These samples ranged from municipal secondary sewage effluent and river water to municipal tap water.

High correlation coefficients were obtained for water samples which contained sufficient organic carbon to permit accurate TOC determinations. Predictably, systems with low TOC levels yielded lower correlation coefficients. However, even with the lower correlation coefficients, absorbance measurements can still be used to monitor a process stream for its organic carbon content if interferences from turbidity do not exceed certain limits.

1

THE USE OF ULTRAVIOLET ABSORBANCE FOR MONITORING THE TOTAL ORGANIC CARBON CONTENT OF WATER AND WASTEWATER

Richard A. Dobbs, Robert H. Wise and Robert B. Dean*

A rapid combustion method for measuring the total organic carbon (TOC) content of water has been described by Van Hall and coworkers (1963). Their method has been incorporated into a commercial instrument, the Beckman Carbonaceous Analyzer (1967). Williams (1967) has described the use of this instrument as a water pollution research tool and has correlated the Analyzer's carbon values with those obtained by the more conventional Chemical Oxygen Demand and Biochemical Oxygen Demand tests. The relatively high cost of the Carbonaceous Analyzer, however, has prompted an attempt to find a low-cost instrument for monitoring organics in water.

An alternate analytical approach, which seemed to have considerable potential as a monitor for organics, is based on the fact that many pollutants commonly found in water strongly absorb ultraviolet radiation. Wedgwood (1952) suggested using ultraviolet absorbance measurements at 366 m μ to "assess the quality of an effluent." This wavelength was chosen because it coincides with one of the sharp spectral lines of the low-pressure mercury lamp. Hoather (1953) measured the absorbance between 210 m μ and 700 m μ on a variety of waters and recommended a wavelength of 275 m μ and a cell length of 4 to 20 cm, depending on the degree of water contamination. The effect of various physiochemical processes in removing organic contaminants from polluted river water was described by Dornbush and Ryckman (1962). Among the analytical methods applied to the process effluents were absorbance measurements over the

* Richard A. Dobbs, Research Chemist, Physical & Chemical Treatment Research Program, Advanced Waste Treatment Research Laboratory, Cincinnati, Ohio.
Robert H. Wise, Chemist, Contracts & Grants Activities, Advanced Waste Treatment Research Laboratory, Cincinnati, Ohio.
Robert B. Dean, Chief, Ultimate Disposal Research Program, Advanced Waste Treatment Research Laboratory, Cincinnati, Ohio.

200 to 285-m μ region. These authors recommended absorbance measurements at 250 m μ as a useful parameter which could "permit evaluation of removals of the soluble trace organic pollutants by physiochemical processes." Ultraviolet absorbance at 253.7 m μ was employed by Bramer et al. (1966) to monitor both the effluent from a chemical plant producing coal-based chemicals and the still-waste effluent from a coke plant. Recently, Briggs and Melbourne (1967) presented limited data on the relationship between the absorbance at 253.7 m μ and the organic carbon content of water from six different rivers and three different sewage plant effluents.

Ultraviolet Absorbance Measurements For Monitoring The Carbon Adsorption Process

Early in 1965, the Advanced Waste Treatment Research Program began a pilot-plant investigation of the adsorption of soluble organics from secondary treatment plant effluent onto granular activated carbon (1967). The operation of this pilot plant provided an excellent opportunity to evaluate the relationship between ultraviolet absorbance and TOC under well-controlled conditions. In order to select a suitable wavelength for measuring these ultraviolet absorbances, a sample of secondary effluent was scanned before and after granular carbon treatment. The resulting spectrum is shown in Figure 1. Ultraviolet absorbance increased with decreasing wavelength but showed only a gradual change in the 240 to 270-m μ region of the ultraviolet. Since this plateau includes the strong and sharp 253.7-m μ spectral line of the low-pressure mercury lamp, that particular wavelength was chosen for the absorbance measurements.

The carbon adsorption pilot plant was operated continuously for 258 days. During this period, grab samples were collected daily for TOC determinations using the Beckman Carbonaceous Analyzer, and for ultraviolet absorbance

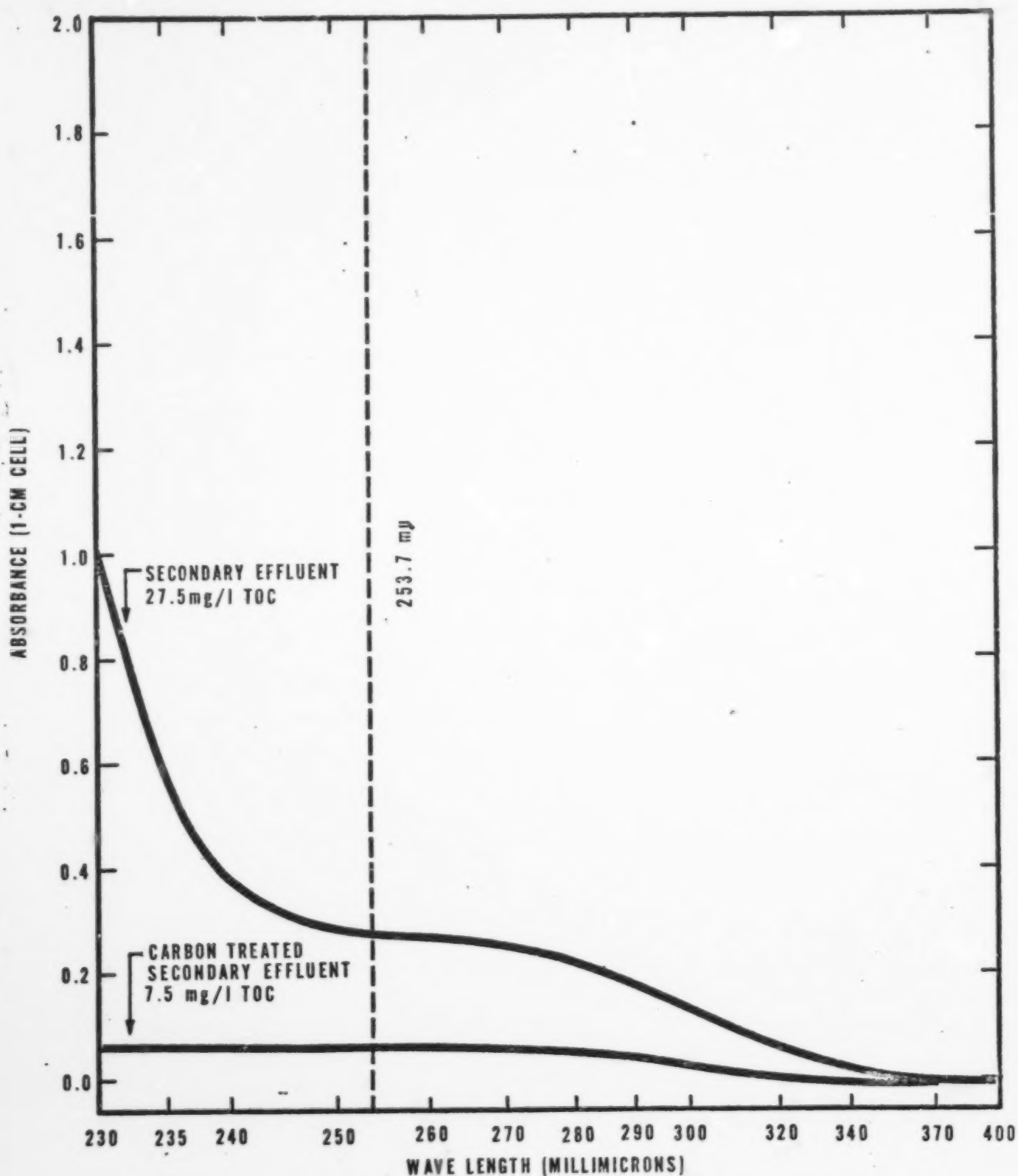


FIGURE 1. ULTRAVIOLET SPECTRA OF MUNICIPAL SECONDARY EFFLUENT BEFORE AND AFTER CARBON TREATMENT.

($A_{254 \text{ m}\mu}^{1 \text{ cm}}$) measurements at 254 $\text{m}\mu$ using a Beckman DU Spectrophotometer.

A 1-cm cell was used for absorbance measurements in the pilot-plant study because the time required to collect sufficient sample from each carbon depth for a larger cell would have been excessive. Samples of the clarified secondary-effluent column feed, the effluent from the 12, 24, 36, and 48-inch depths of carbon and the total column effluent were analyzed. During the pilot-plant study, segments of the carbon column were replaced periodically with fresh carbon by removing top segments and adding equal numbers of new carbon segments at the bottom so as to keep the overall column length constant.

A "simple linear regression" on the data from each sampling point was performed after completion of the experimental phase. The pertinent computer results are shown in Table I.

The fact that the pooled data (excluding the column feed values and total column effluent values) yielded a correlation coefficient as good as, or better than, the individual coefficients strongly suggests that a single linear function adequately represents the relationship of $A_{254 \text{ m}\mu}^{1 \text{ cm}}$ to TOC for the 12, 24, 36, and 48-inch depths of carbon.

Simple linear regression results were also obtained for the total column effluent after it had contacted the entire 120-inch bed of activated carbon. Since the entire carbon-column flow was available for sampling purposes, absorbance measurements were made using a 5-cm cell. For the systems considered in the present investigation, the absorbance values obtained using a 5-cm cell are to the first approximation five times as great as the values one would have measured using a 1-cm cell. The correlation coefficient obtained for the total carbon-column effluent was smaller than the corresponding values for the intermediate sampling points. After the effluent had contacted the entire 120-inch carbon bed, the effluent TOC

TABLE I

"Simple Linear Regression" Results for A 1 cm and TOC from the Carbon-Adsorption Pilot Plant

Carbon Depth (Inches)	Average U.V. Absorbance 1 cm A 254 m μ	Average TOC (mg/l)	Number Observations (N)	Slope (TOC/A)	Intercept (TOC)	Correlation Coefficient
0	0.107	7.79	236	56.6	1.73	0.85
12	0.085	6.87	235	75.0	0.53	0.91
24	0.069	5.87	234	84.4	0.07	0.93
36	0.056	4.88	236	81.0	0.32	0.93
48	0.050	4.52	206	79.5	0.54	0.89
12 to 48-inch depths pooled	0.065	5.57	911	80.0	0.39	0.93
120	0.098*	2.0	45	10.8*	0.90	0.60

* Absorbance values were measured in a 5-cm cell; in order to correct to 1-cm cell values, the slope would be multiplied by approximately 5.

and $A_{254\text{ m}\mu}^{5\text{ cm}}$ values were extremely low. The "average" TOC of 2.0 mg/l and $A_{254\text{ m}\mu}^{5\text{ cm}}$ of 0.098 actually represent selected values for the total column effluent since many of these TOC values were below the lower detectable limit of the Beckam Carbonaceous Analyzer and could not be used in the computer program. More accurate absorbance values could have been measured using a cell path longer than 5 cm, but no corresponding (i.e., more accurate) values for the TOC would have been available.

Survey of Municipal Wastewater Treatment Plants

Encouraged by the results from the carbon-adsorption pilot plant, attempts were made to evaluate the $A_{254\text{ m}\mu}^{5\text{ cm}}$ -TOC correlation for other aqueous samples. Secondary effluent samples from six different municipal plants were collected on three different dates during the summer months. All of these samples were filtered through glass-fiber filter paper to remove particulate matter, then a portion of each filtered effluent was further clarified by flocculation with 400 mg/l of Ca(OH)_2 . $A_{254\text{ m}\mu}^{5\text{ cm}}$ and TOC measurements were made on the filtered effluents before and after lime clarification. Computer program results are summarized in Table II.

The correlation coefficient of 0.87 for the six different lime-clarified secondary effluents agrees very well with the value of 0.85 obtained for the clarified secondary effluent used as column feed in the carbon-adsorption pilot-plant study. More importantly, the high correlation coefficient for the combined data from all six municipal treatment plants is further indication that the close relationship between $A_{254\text{ m}\mu}^{5\text{ cm}}$ and TOC is reasonably universal and not a unique characteristic of a single treatment plant.

TABLE II

"Simple Linear Regression" Results for Municipal Secondary Effluents

Sample Identification	Average U.V. Absorbance (A 254 _{ml})	Average TOC (mg/l)	Number Observations (N)	Slope (TOC/A)	Intercept (TOC)	Correlation Coefficient
Glass-Fiber* -Filtered Secondary Effluent	1.30	17.1	16	12.7	0.53	0.84
Filtered* and Lime-Clarified Secondary Effluent	0.711	11.6	27	15.7	0.41	0.87

* No. 1106 BH manufactured by Mine Safety Appliances Company, Pittsburgh, Pa.

Monitoring of Raw and Processed River Water

The Mega Sampler described by Middleton (1962) was designed to recover organic contaminants from polluted water. The water to be sampled is passed through a sand filter, followed by a column of activated carbon. The adsorbed materials are later removed by extraction - first with chloroform, then with alcohol. The concentrating of each extract by distillation leaves a residue of organics for additional study.

During the present investigation, the Mega Sampler was operated at two sampling stations on the Great Miami River. Samples of the raw, sand-filtered only, and sand-filtered plus carbon-treated river water from both stations were collected. All samples were filtered through 0.45- μ Millipore membranes, then $A_{254}^{5\text{ cm}}$ and TOC were determined. Computer results are shown in Table III. The pooled data from each station yielded a correlation coefficient greater than that for any one individual type of sample. In order to determine whether or not the slopes of the regressions summarized in Table III were statistically equivalent, an analysis of covariance was performed. A computer program written in Fortran II was used. The hypothesis of homogeneity of regression coefficients is accepted when $F < F_{\alpha}$ and rejected when $F > F_{\alpha}$, where F_{α} is the tabulated value with $(K-1)$ and $(N-2K)$ degrees of freedom (K being the number of regressions, and N being the total number of data values in all the regressions) and where α is the probability of rejecting the null hypothesis. The computed F value was indeed less than the tabulated value, F_{α} , at the 99% confidence level. Therefore, the slopes are not significantly different, and all the data can be represented by a single line or slope. A plot of $A_{254}^{5\text{ cm}}$ versus TOC for the Mega Sampler data is shown in Figure 2. The dashed lines represent one standard deviation for the experimental TOC values represented by the solid regression line. Approximately 97% of the values fall within one standard deviation of the regression line.

TABLE III

"Simple Linear Regression" Results for Mega Sampler Data

Station	Sample	Average U.V. Absorbance (A 5 cm 254 mμ)	Average TOC (mg/l)	Observations (N)	Slope (TOC/A)	Intercept (TOC)	Correlation Coefficient
Hamilton, Ohio	Raw River Water	0.482	5.6	13	4.9	3.3	0.44
	Sand-filtered	0.465	5.3	13	7.8	1.7	0.84
	Carbon-treated	0.236	3.0	13	8.2	1.1	0.92
	Samples-Pooled	0.394	4.6	39	9.4	1.0	0.93
Clevs, Ohio	Raw River Water	0.479	4.9	16	16.0	-2.6	0.50
	Sand-filtered	0.442	4.3	16	7.9	0.8	0.82
	Carbon-treated	0.230	2.9	16	4.8	1.8	0.52
	Samples-Pooled	0.383	4.0	48	7.5	1.1	0.86
All Data Pooled		0.389	4.3	87	8.5	1.0	0.88

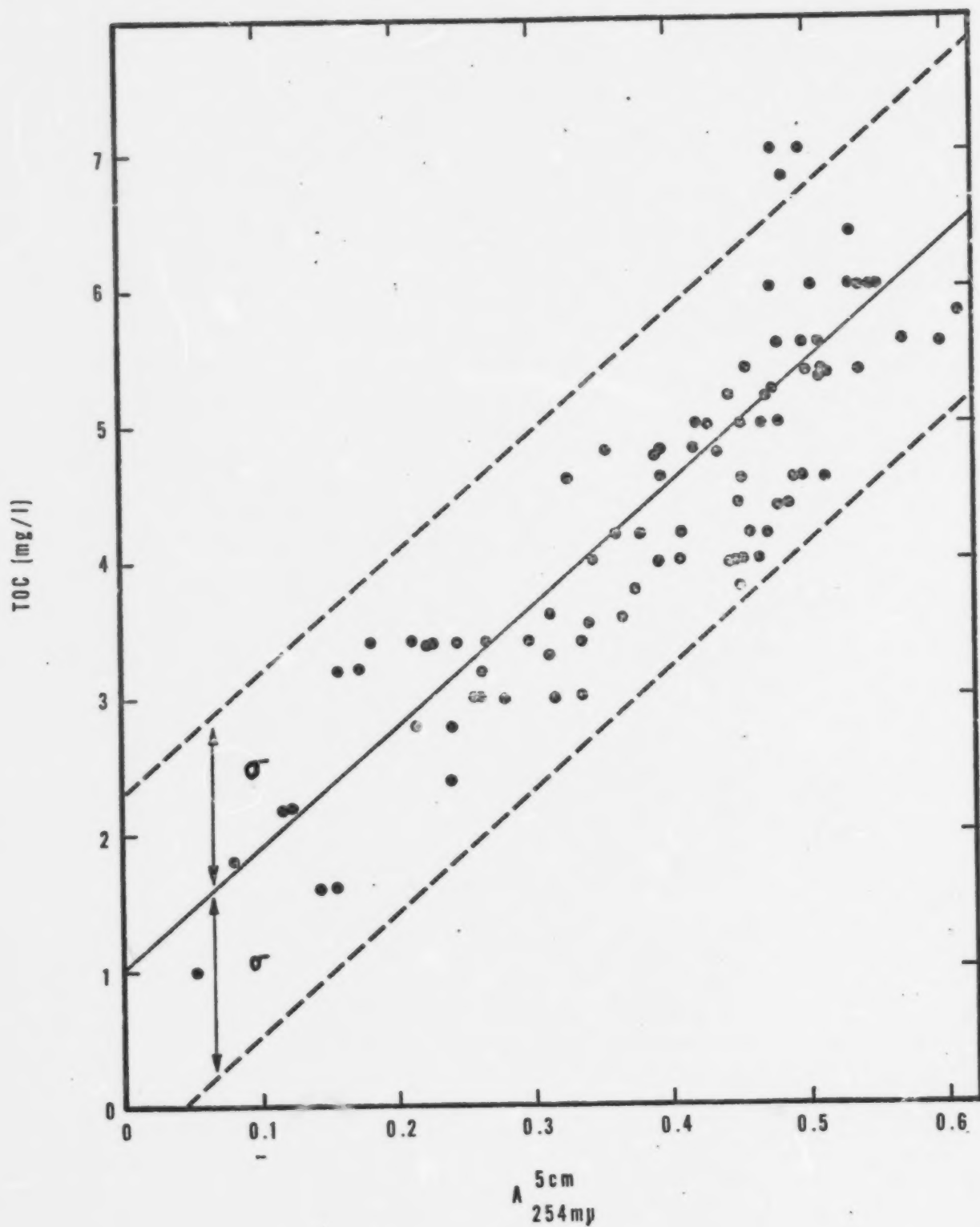


FIGURE 2. TOTAL ORGANIC CARBON VERSUS ULTRAVIOLET ABSORBANCE FOR MEGA SAMPLER DATA.

Municipal Water-Treatment Plant Survey

A municipal water-treatment plant was surveyed to determine the correlation between $A_{254}^{5\text{ cm}}$ and TOC for water at various stages of processing. A schematic flow diagram of the plant is shown in Figure 3. Samples of the raw river water, the influent to the second chemical house, and the finished water (tap water) were collected and filtered through 0.45- μ Millipore membranes. $A_{254}^{5\text{ cm}}$ and TOC were both measured for eleven different sets of samples collected over a four-month period. Under these conditions, sampling should reflect changes in river stages and in treatment requirements at the municipal plant. Computer results for the municipal water-treatment plant survey are shown in Table IV. Analysis of covariance again showed that the slopes of the regressions for the different stages of treatment are not significantly different. A plot of the pooled data is shown in Figure 4. Although the correlation coefficients are lower than those obtained for other systems, the relationship between $A_{254}^{5\text{ cm}}$ and TOC is still a useful one. The dashed lines again represent one standard deviation (i.e., 0.66) in the TOC measurements, and approximately 79% of the data points fall within one standard deviation of the solid regression line. However, almost 94% of all the data points fall within plus-or-minus one TOC unit of the regression line.

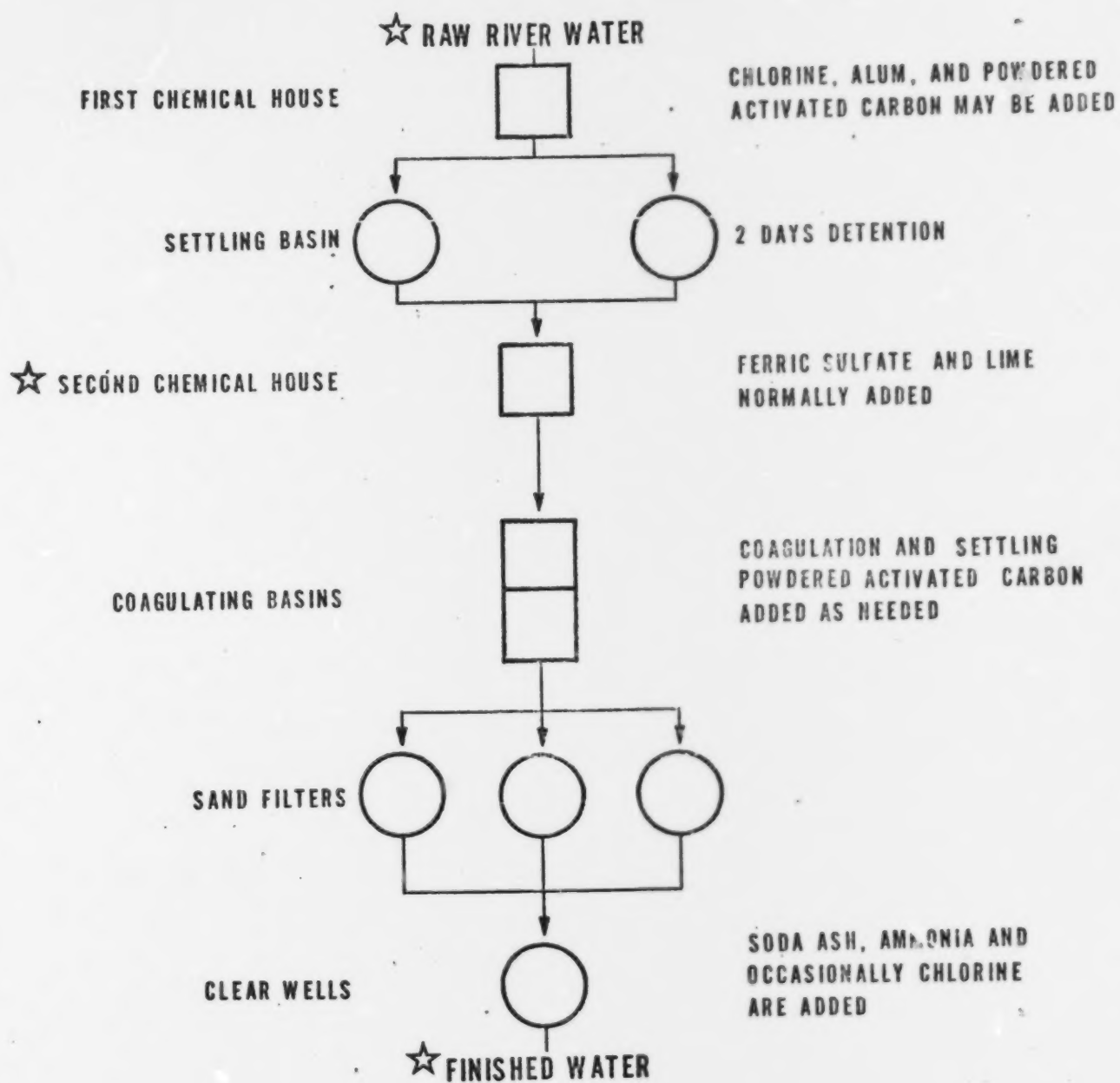
Effect of Turbidity On Ultraviolet Absorbance Measurements

In order to maintain a useful correlation between $A_{254}^{5\text{ cm}}$ and TOC for aqueous samples, turbidity must not exceed certain limits. According to Oster (1950), the total light scattered by suspended matter increases without limit with increasing particle size when a given number of particles is present; furthermore, the maximum scattering for a given weight of suspended matter occurs when the particle size is approximately equal to the wavelength

TABLE IV

"Simple Linear Regression" Results for a Municipal Water-Treatment Plant

Sampling Station	Average U.V. Absorbance ($A_{5\text{ cm}}$) (254 mμ)	Average TOC (mg/l)	Number Observations (N)	Slope (TOC/A)	Intercept (TOC)	Correlation Coefficient
Raw River Water	0.316	3.2	11	2.32	2.44	0.19
Second Chemical House Influent	0.258	3.0	11	7.63	1.02	0.51
Finished Water	0.196	2.6	11	11.71	0.29	0.61
All Data Pooled	0.257	2.9	33	5.24	1.57	0.51



★ SAMPLING STATIONS

FIGURE 3. SCHEMATIC FLOW DIAGRAM OF
MUNICIPAL WATER-TREATMENT PLANT

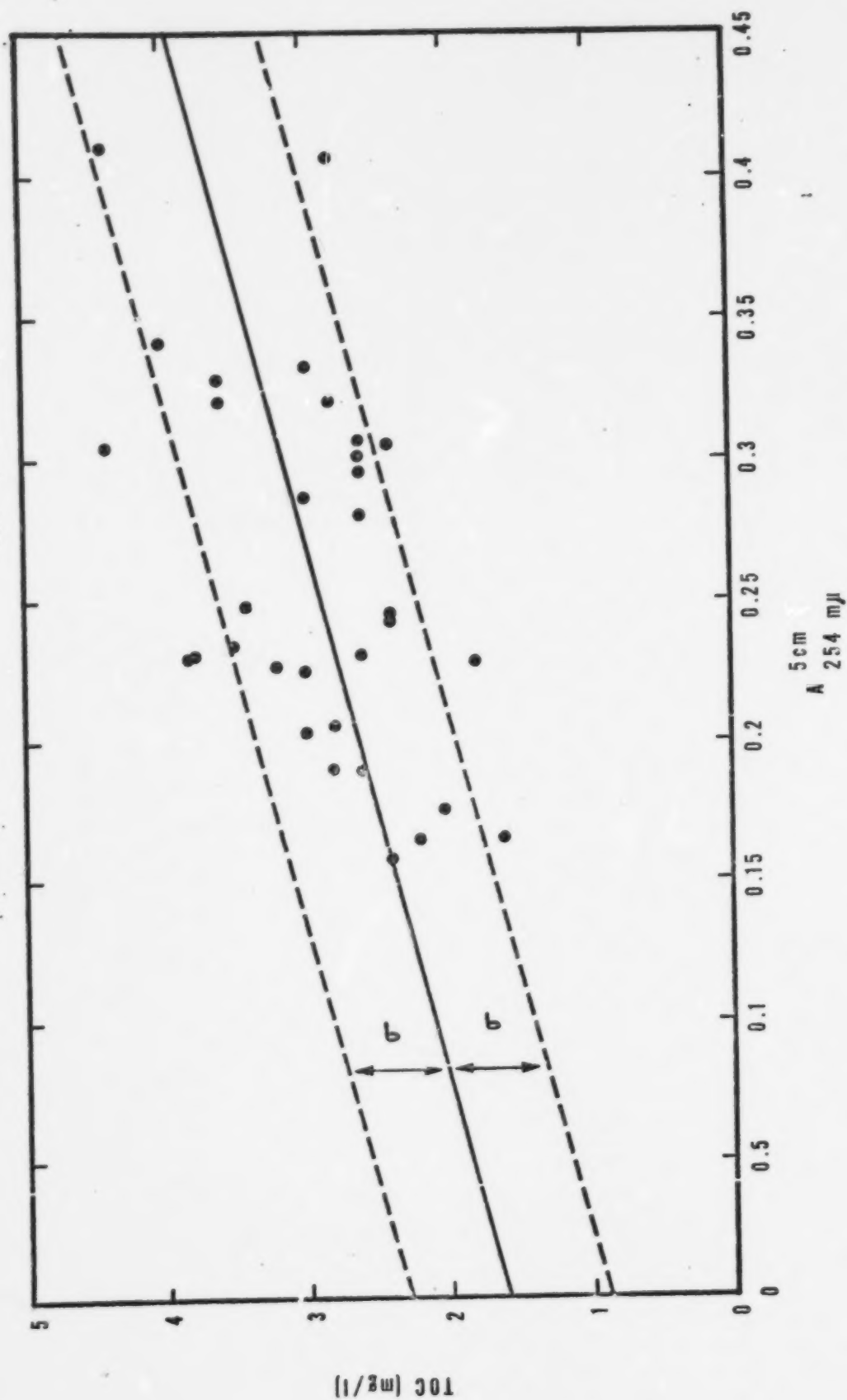


FIGURE 4. TOTAL ORGANIC CARBON VERSUS ULTRAVIOLET ABSORBANCE
FOR MUNICIPAL WATER-TREATMENT PLANT SURVEY.

of the incident light. Therefore, the extent to which turbidity will affect the ultraviolet absorbance measurement will depend on both the number and size of the suspended particles. A corollary of this statement is that U.V. radiation is scattered to a much greater degree by particles of "colloidal" size, (i.e., less than 500-m μ diameter) than is radiation of longer wavelengths.

The effect of turbidity on the correlation between A $\frac{5 \text{ cm}}{254 \text{ m}\mu}$ and TOC was eliminated in the present investigation by making all measurements on filtered samples. Nevertheless, some estimate of the interference caused by turbidity was considered desirable, particularly to permit assessment of the feasibility of continuous ultraviolet monitoring of a process stream. In order to estimate the interference caused by turbidity for municipal wastewater, two different secondary sewage effluents were filtered through five different pore-size Millipore membranes in parallel filters (water-soluble components were leached from the membranes with distilled water prior to use).

A $\frac{5 \text{ cm}}{254 \text{ m}\mu}$ and TOC values were measured for each filtrate. Corresponding turbidity values were determined using a "Model 1860" Hach turbidimeter. Analytical results are summarized in Table V. The absorbance equivalent to one Jackson Turbidity Unit (JTU) was calculated from the data presented in Table V. An "overall effect" was calculated by comparing the unfiltered values with those obtained for the 0.1- μ filtrates; this effect is shown in Table VI.

An additional test was conducted in an effort to obtain a "model" for the effect of turbidity on the A $\frac{5 \text{ cm}}{254 \text{ m}\mu}$ measurement. A colloidal silica, stock solution was prepared by diluting 1.0 ml of duPont "Ludox" to 100 ml with distilled water. A second stock solution contained 225 mg of bentonite powder in one liter of distilled water. Serial dilutions were prepared from each stock solution for measurements of turbidity and absorbance. Plots of

TABLE V

Effect of Millipore Filtration on Turbidity, Absorbance, and Total Organic Carbon

Millipore Pore-Size (microns)	Turbidity, Jackson Turbidity Units (JTU)		$A_{254}^{5\text{ cm}}$		TOC (mg/l)	
	Effluent #1	Effluent #2	Effluent #1	Effluent #2	Effluent #1	Effluent #2
(Unfiltered)	6.50	4.20	0.790	0.875	7.4	11.4
1.5	0.41	0.35	0.563	0.752	6.2	10.0
0.8	0.12	0.18	0.526	0.711	5.8	8.8
0.45	0.11	0.13	0.521	0.698	5.6	8.4
0.3	0.06	0.07	0.505	0.691	5.2	8.4
0.1	0.06	0.07	0.508	0.687	5.2	8.4

the data were linear, up to approximately 7.0 JTU, for both sets of synthetic solutions. The absorbance units which correspond to one JTU are 0.060 and 0.130 for silica and bentonite, respectively.

TABLE VI

Absorbance Equivalent Due to One Jackson Turbidity Unit

Overall Effect,
Unfiltered vs 0.1 μ filtrate

	<u>Effluent #1</u>	<u>Effluent #2</u>
$\Delta A \frac{5 \text{ cm}}{254 \text{ m}\mu}$	0.282	0.188
ΔJTU	6.44	4.13
$\Delta A \frac{5 \text{ cm}}{254 \text{ m}\mu}$	0.044	0.046
ΔJTU		

Discussion and Conclusions

A useful correlation has been demonstrated between ultraviolet absorbance and TOC content for numerous aqueous systems. Turbidity of any given water sample must not exceed a certain limit if the correlation is to be useful; in turn, that limit will depend on the absolute absorbance value of the water being measured.

High correlation coefficients were obtained for municipal secondary effluent for which the concentration of TOC could be determined with considerable accuracy. Aqueous samples with TOC levels near the lower detectable limit of the Beckman Carbonaceous Analyzer gave lower correlation coefficients. Even though these latter correlation coefficients were smaller, the relationship between $A_{254}^{5\text{ cm}}$ and TOC should still be useful for certain monitoring purposes. At the present, absorbance measurements may give a more reliable indication of the organic carbon in some low-level samples than would TOC determinations. The future availability of a more sensitive carbonaceous analyzer would furnish better data for calculating more reliable correlations for low-level samples.

High concentrations of inorganic ultraviolet absorbers or high concentrations of organics which do not absorb in the ultraviolet will adversely affect the correlation between $A_{254}^{5\text{ cm}}$ and TOC. Generally, these conditions do not represent a problem in the monitoring of natural water systems; however, in the case of certain industrial wastes or mixed municipal-industrial wastes this problem may be encountered. A few preliminary comparisons of TOC with $A_{254}^{5\text{ cm}}$ should indicate whether or not the proposed monitoring technique is applicable.

The use of ultraviolet absorbance to monitor the concentration of organics in water has numerous advantages over alternate methods. Equipment design can be either simple or sophisticated. The low-pressure mercury lamp has a sharp spectral line at 253.7 mμ which, when appropriately filtered, provides a low-cost monochromatic light source. Absorbance values can be displayed on a meter, or they can be recorded to provide a permanent record. Sensitivity can be adjusted to monitor a wide range of organic concentrations by varying the length of the sample cell. Application of ultraviolet monitors is simple and does not require the services of a skilled operator. The units can be completely self-contained with their own power supply so that remote locations, which would otherwise be difficult to survey, can be monitored.

Acknowledgement

We acknowledge the assistance of Robert Smith, Ella Hall and Richard Eilers for the statistical evaluation of the data presented. The authors also wish to acknowledge the analytical services provided by Robert Williams.

LITERATURE CITED

Beckman Instruments, Inc., Scientific and Process Instruments Division,
Fullerton, California, Bulletin 4082 (1967).

Bishop, D. F., Marshall, L. S., O'Farrell, T. P., Dean, R. B., O'Connor, B.,
Dobbs, R. A., Griggs, S. H. and Villiers, R. V., JWPCF, 39 (2), 188-203 (1967).

Bramer, H. C., Walsh, M. J. and Caruso, S. C., Wat. Sewage Wks., 113, 275-78
(1966).

Briggs, R. and Melbourne, K. V., "Recent Advances in Water-Quality Monitoring."
Presented at the Meeting of Society for Water Treatment & Examination,
September 21, 1967.

Dornbush, J. N. and Ryckman, D. W., "The Effects of Physiochemical Processes
in Removing Organic Contaminants." Presented at the 35th Annual Meeting,
Water Pollution Control Federation, Toronto, Canada, October 7-11, 1962.

Hoather, R. C., Proc. Soc. Water Treatment & Examination, 2, 9-22 (1953).

Middleton, F. M., Pettit, H. H. and Rosen, A. A., Engineering Bulletin of Purdue
University, Proc. of the 17th Industrial Waste Conf., Engineering Extension Series,
Series No. 112, 454-60 (1962).

Oster, G., Chem. Rev., 43, 319-65 (1950).

Van Hall, C. E., Safranko, J. and Stenger, V. A., Anal. Chem., 35, 315-19 (1963).

Wedgwood, P., J. Inst. Sewage Purif., Part 1, 20-31 (1952).

Williams, R. T., Instrumentation Technology, 14 (2), 63-66 (1967).